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Electronic Supporting Information

Radiation sensitive hybrid polymer based on Mn-Anderson polyoxometalate cluster and a UV active organic monomer: synergistic effects lead to improved photocurrent in a photoresponse device

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Materials and Instrumentation

Triethylamine and acetonitrile were distilled over CaH_2 and acetonitrile was stored over 4 Å molecular sieves prior to the use. The MAPDST monomer, its homopolymer and methacryloyl chloride were synthesized according to the literature procedure.[1] AIBN (2,2′-azobis(2-methylpropionitrile)) was purified via recrystallisation in methanol prior to the use. Spectroscopic grade chloroform was used as received from Merck. The tris(hydroxymethyl)aminomethane (TRIS) grafted Mn-Anderson cluster, $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]$, **1,** was synthesized according to the reported procedure.[2] Methacryloyl group grafted organic-POM hybrid monomer $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3CNHCO(CH_3)C{=}CH_2\}_2]$ (**2**), was synthesized by refluxing the acetonitrile solution of compound **1** with methacryloyl chloride in presesnce of triethylamine. Formation of compound **2** was confirmed by comparing its analytical and spectroscopic data with literature report.[3] POM-MMA hybrid polymer was synthesized following a reported procedure.[4]

The ^{1}H NMR spectra were recorded on a 500 MHz JEOL JNM instrument in DMSO-d_6 /$CDCl_3$ solvent. FT-IR spectra were obtained from samples dispersed in KBr pellets using Perkin Elmer, Spectrum 2 Spectrophotometer. Thermogravimetric analyses (TGA) were done on a Netzsch Model STA 449 F1 JUPITER instrument at a heating rate of 10 °C/min under N_2 atmosphere. Gel-permeation chromatography (GPC) analysis of the hybrid polymer was conducted on PL gel mixed-C 5 µm columns, using Agilent Technologies 1260 Infinity Series instrument. DMF with 0.1% LiBr was used as a mobile phase at a flow rate of 1 mL/min and the molecular weight was determined by using PEO and PEG standards. Thickness of the POM/polymer hybrids and MAPDST homopolymer films in the devices were measured by a Bruker Optical Profiler (GTK-14-0161). Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis of the sample were performed using a FEI Tecnai G2 20 S-Twin microscope operating at 200 kV.

Synthesis of POM-MAPDST Hybrid Polymer

A typical free-radical polymerization was carried out as follows: in a dry Schlenk flask, organic-POM hybrid monomer (0.1 g, 0.048 mmol), MAPDST monomer (0.9 g, 2.41 mmol), AIBN (10 mg, 0.060 mmol) and dry acetonitrile (3 mL) were added under N_2 atmosphere. After three freeze-pump-thaw cycles, the flask was placed in a constant temperature oil bath at 70 °C for 2 days. The polymerization was stopped by cooling the flask to room temperature. The viscous reaction mixture thus obtained was slowly added into excess of diethyl ether with constant stirring to give a light orange colored precipitate. The obtained solid was washed thrice with ether and dried in a temperature controlled hot air oven at 40 °C for 24 h. Yield: 690 mg, 69 %. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H = 8.04 (2H, s br, *m,m′*-ArH), 7.43 (2H, s br, *o,o′*-ArH), 3.23 (6H, s, $S(CH_3)_2$), 1.8-2.8 (2H, br peak, CH_2), 1.0-1.7 (3H, br peak, CH_3); IR (KBr pellet, v/cm^{-1}): 3111, 3027, 2939 (C−H), 1754 (C=O), 1213, 1255 (C-F), 948, 927 (Mo=O), and 807, 636 (Mo-O-Mo) vibrations. ^{19}F NMR (500 MHz, DMSO-d_6): δ_F = -77.6 (3F, s, CF_3). GPC (DMF + 0.1 % LiBr, eluent): M_w = 6312, M_n = 4114, PDI = 1.53.

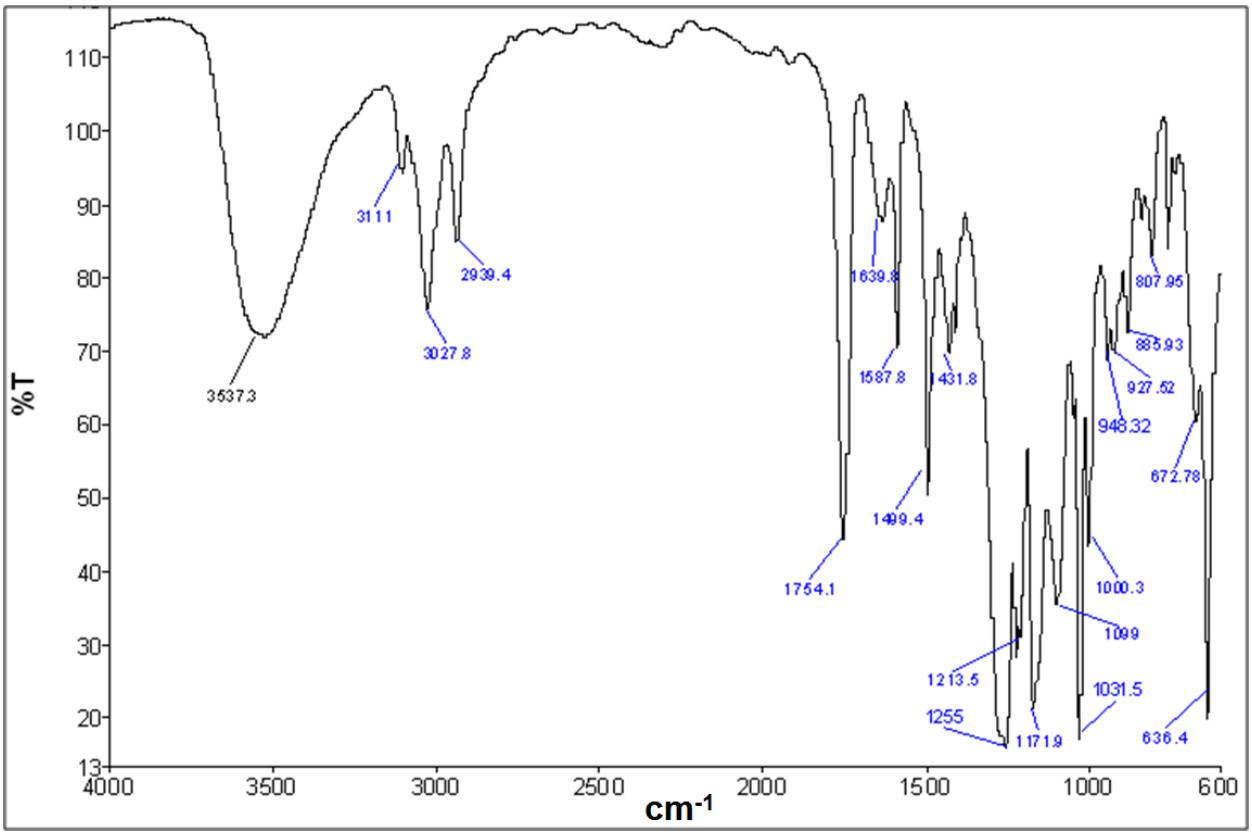
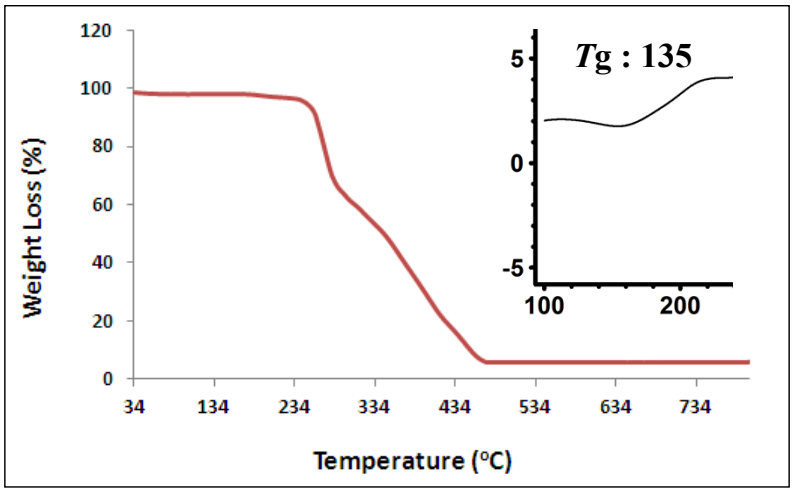


Figure S1. IR spectrum of POM-MAPDST hybrid polymer

Fabrication and Characterization of Devices

ITO coated glass substrates (Sigma Aldrich, sheet resistance 8-12 Ω/sq) were cleaned with a special detergent followed by ultra-sonication in deionized water, acetone and isopropyl alcohol. Dried in an oven at 100 ^{o}C for 30 min. The POM-MAPDST hybrid polymer and MAPDST homopolymer (0.8 wt %) solutions in acetonitrile and POM-MMA hybrid polymer (0.8 wt %) in anisole solvent were prepared and spin coated on the ITO coated glass substrates with a spinning rate of 5000 rpm for 60 s to achieve a thickness of ~70 nm. The films of the polymer were dried and a layer of Al (70 nm thick) was deposited over it using a thermal evaporator at a vacuum of 10^{-6} torr. The photocurrent was measured using Keithley 2400 source meter unit under simulated 100 mW/cm^2 AM1.5G irradiation (wavelength range of the filter: 350-1800 nm) from an OAI Trisol solar simulator calibrated with a standard Si solar cell.



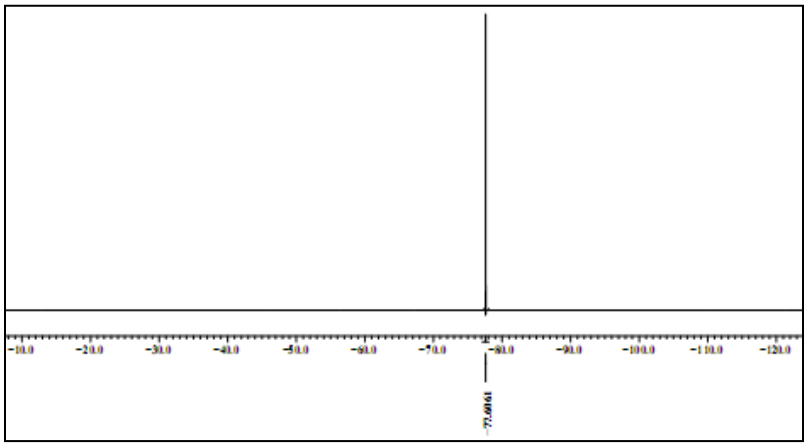


Figure S2. (**(a)**, above) Thermo gravimetric (TG) curve (Inset: DSC curve after first heating cycle) at a heating rate of 10 °C/min under N_2 atmosphere and (**(b)**, below) ^{19}F NMR spectra of the POM-MAPDST hybrid polymer in DMSO-d_6.

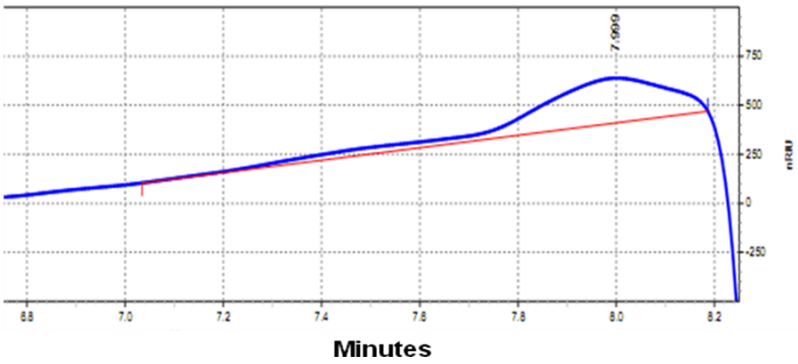


Figure S3. GPC curve of the POM-MAPDST hybrid polymer in DMF solvent (0.1 % LiBr) at a flow rate of 1 ml/min

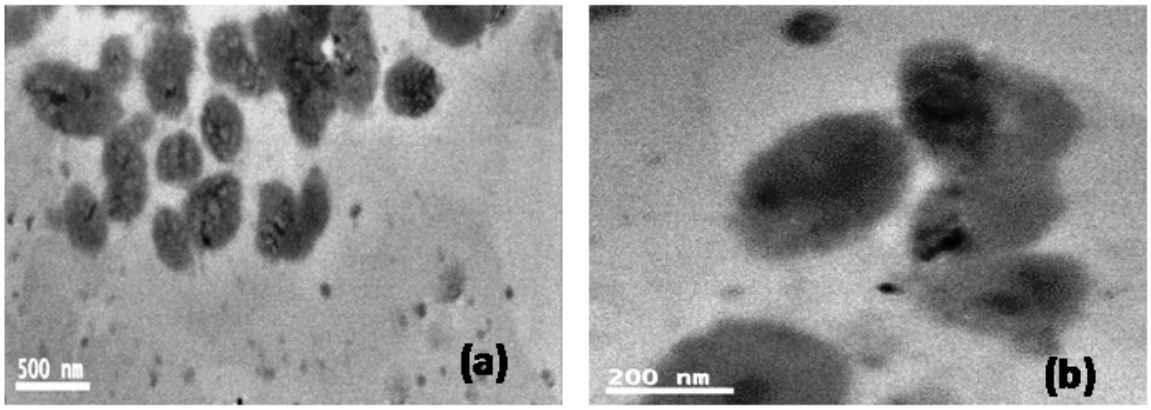
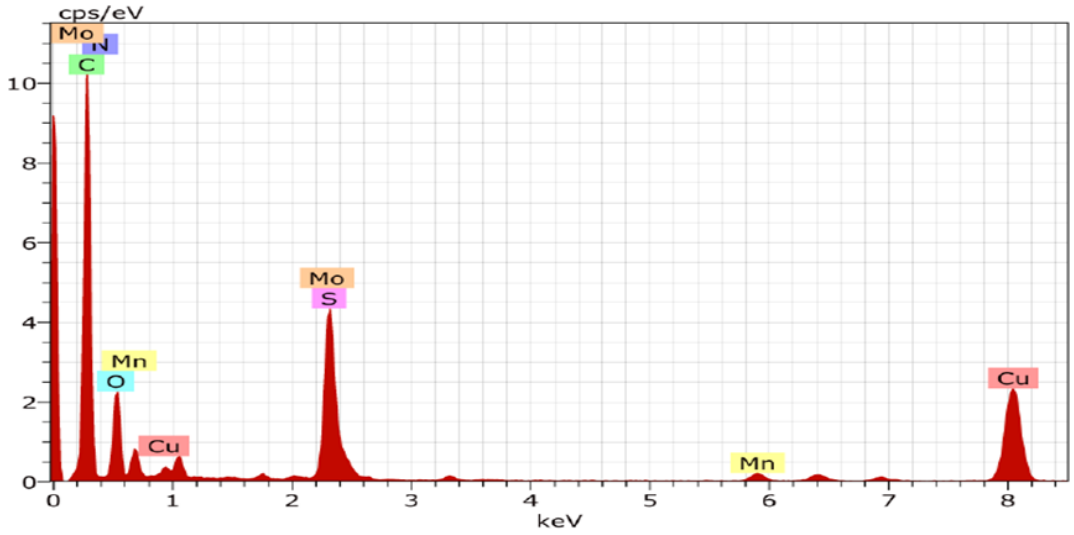


Figure S4. TEM images of the POM-MAPDST hybrid polymer. Drop cast from the dispersion of POM-MAPDST hybrid polymer in H_2O. (a) is showing agglomerates of particles ranging from 200 to 250nm.



Element	Series	Net unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Copper	K-series	40592	7.15	1.55	0.73
Carbon	K-series	59291	81.91	93.93	7.52
Nitrogen	K-series	443	0.17	0.16	0.10
Oxygen	K-series	12775	2.52	2.17	0.31
Sulfur	K-series	30733	3.35	1.44	0.38
Manganese	K-series	2414	0.38	0.10	0.12
Molybdenum	K-series	5381	4.53	0.65	0.53
	Total:	100.00	100.00	100.00	

Figure S5. EDX analysis showing signals of molybdenum, manganese, sulfur etc. elements in the POM-MAPDST hybrid polymer. The analysis was done on Cu grids. The weight percentage of Mo : Mn is calculated to be (11.9 : 1) which is near to the calculated value (10.46 : 1) expected for Mn-Anderson cluster.

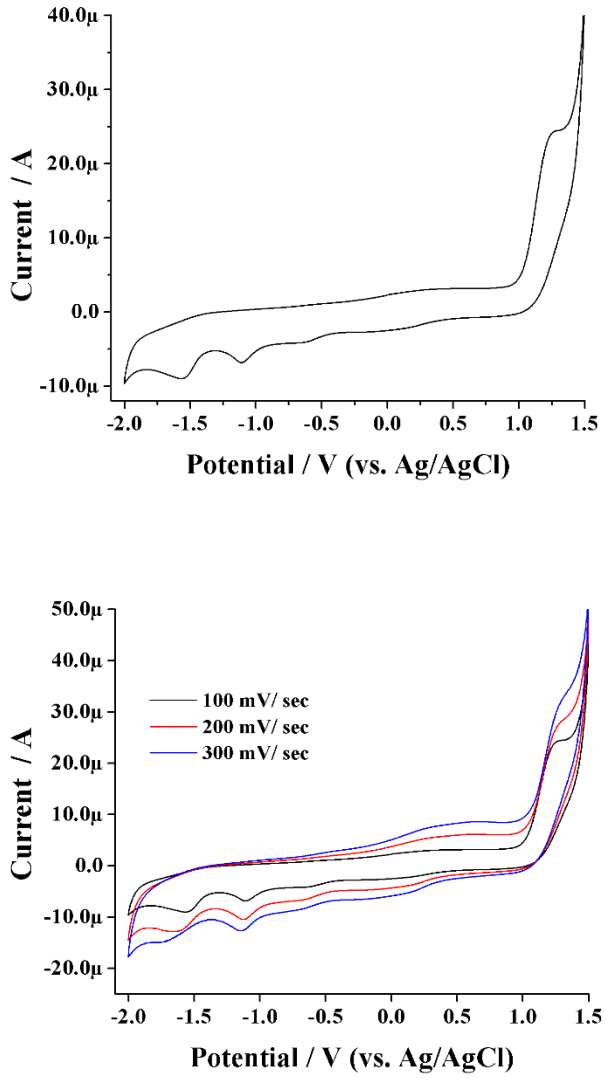


Figure S6. The cyclic voltammogram of POM-MAPDST hybrid polymer in DMSO solutions at 100 mV/s scan rate (above) and at 100, 200, 300 mV/s scan rates (below). The oxidation peak corresponding to Mn (III) to Mn (IV) appears at 1.2 V. Two peaks appearing at -1.15 and -1.6 could be due to the reduction of Mn(IV) and Mn(III) species. Experimental conditions: solvent-DMSO, electrolyte - tetra butyl ammonium hexafluorophosphate, working electrode - glassy carbon, reference electrode-Ag/AgCl, counter electrode - Pt wire.

References

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2. P. R. Marcoux, B. Hasenknopf, J. Vaissermann and P. Gouzerh, *Eur. J. Inorg. Chem.,* 2003, **2003**, 2406-2412.
3. B. Hu, C. Wang, J. Wang, J. Gao, K. Wang, J. Wu, G. Zhang, W. Cheng, B. Venkateswarlu, M. Wang, P. S. Lee and Q. Zhang, *Chem. Sci.,* 2014, **5**, 3404-3408.
4. B.Hu, C. Wang, J. Wang, J. Gao, K. Wang, J. Wu, G. Zhang, W. Cheng, B. Venkateswarlu, M. Wang, P. S. Lee and Q. Zhang, *Chem. Sci.,*2014, **5**, 3404-3408.